Dossier

This paper is a part of the hereunder thematic dossier published in OGST Journal, Vol. 68, No. 2, pp. 187-396 and available online here

Cet article fait partie du dossier thématique ci-dessous publié dans la revue OGST, Vol. 68, n°2, pp. 187-396 et téléchargeable ici

DOSSIER Edited by/Sous la direction de : **Jean-Charles de Hemptinne**

InMoTher 2012: Industrial Use of Molecular Thermodynamics
InMoTher 2012 : Application industrielle de la thermodynamique moléculaire

Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 68 (2013), No. 2, pp. 187-396

IFP Energies nouvelles

Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 68 (2013), No. 2, pp. 255-270

DOI: 10.2516/ogst/2012088

Dossier

InMoTher 2012 - Industrial Use of Molecular Thermodynamics
InMoTher 2012 - Application industrielle de la thermodynamique moléculaire

Thermodynamic Properties of 1:1 Salt Aqueous Solutions with the Electrolattice Equation of State

A. Zuber[1,2], R.F. Checoni[1], R. Mathew[1], J.P.L. Santos[3], F.W. Tavares[4] and M. Castier[1]*

[1] *Chemical Engineering Program, Texas A&M University at Qatar, Doha - Qatar*
[2] *Departamento de Engenharia Química, Universidade Estadual de Maringá, Maringá, Paraná - Brazil*
[3] *Departamento de Engenharia Química, Universidade Federal do Sergipe, São Cristóvão, Sergipe - Brazil*
[4] *Escola de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro - Brazil*
e-mail: andre.zuber@qatar.tamu.edu - ricardo.checoni@qatar.tamu.edu - rinchu.mathew@qatar.tamu.edu
josepaixaosantos@yahoo.com.br - tavares@eq.ufrj.br - marcelo.castier@qatar.tamu.edu

* Corresponding author, on leave from the Federal University of Rio de Janeiro, Brazil

Résumé — **Propriétés thermophysiques des solutions aqueuses de sels 1:1 avec l'équation d'état de réseau pour électrolytes** — L'équation d'état, dite *électrolattice*, est un modèle qui étend l'équation d'état de Mattedi-Tavares-Castier à des systèmes avec électrolytes. Ce modèle prend en compte l'effet de trois termes. Le premier terme est basé sur les trous dans le réseau en considérant les effets de la composition locale, étude effectuée dans le cadre de la théorie généralisée de Van der Waals : l'équation d'état de Mattedi-Tavares-Castier a été choisie pour ce premier terme. Les deuxième et troisième termes sont les contributions de Born et du MSA. Ils tiennent compte du chargement et du déchargement des ions, et des interactions ioniques à longue distance, respectivement. Le modèle n'ayant besoin que de deux paramètres d'interaction énergétique, il modélise de manière satisfaisante la pression de vapeur et le coefficient d'activité ionique moyenne pour des solutions aqueuses simples contenant du LiCl, LiBr, LiI, NaCl, NaBr, NaI, KCl, KBr, KI, CsCl, CsBr, CsI, ou du RbCl. Deux méthodes pour obtenir les paramètres du modèle sont présentées et mises en contraste : une méthode spécifique pour le sel en question et une autre basée sur les ions. Par conséquent, l'objectif de ce travail est de calculer les propriétés thermophysiques qui sont largement utilisées pour la conception, l'exploitation et l'optimisation de nombreux procédés industriels, parmi eux le dessalement de l'eau.

Abstract *— **Thermodynamic Properties of 1:1 Salt Aqueous Solutions with the Electrolattice Equation of State** — The electrolattice Equation of State (EOS) is a model that extends the Mattedi-Tavares-Castier EOS (MTC EOS) to systems with electrolytes. This model considers the effect of three terms. The first one is based on a lattice-hole model that considers local composition effects derived in the context of the generalized Van der Waals theory: the MTC EOS was chosen for this term. The second and the third terms are the Born and the MSA contributions, which take into account ion charging and discharging and long-range ionic interactions, respectively. Depending only on two energy interaction parameters, the model represents satisfactorily the vapor pressure and the mean ionic activity coefficient data of single aqueous solutions containing LiCl, LiBr, LiI, NaCl, NaBr, NaI, KCl, KBr, KI, CsCl, CsBr, CsI, or RbCl. Two methods are presented and contrasted: the salt-specific and the ion-specific approaches. Therefore, the aim of this work is to calculate thermodynamic properties that are extensively used to design, operate and optimize many industrial processes, including water desalination.*

NOMENCLATURE

List of Symbols

A	Helmholtz free energy
D	Dielectric constant of solution.
D_S	Dielectric constant of pure solvent
e	Elementary charge
$f_i(T)$	Function of temperature
m	Molality of the salt
M	Number of cells of fixed volume v^*
M_s	Molar mass of solvent
nc	Number of components
ng	Number of regions
n	Number of moles
N_a	Avogadro's number
Np	Number of experimental points
OF	Objective function given by Equation (44)
P	Pressure
Q^a	Superficial area of a region of type a
r_i	Volume parameter of component i
R	Universal gas constant
S^m	Area fraction of region of type m on a void-free basis
T	Temperature
u^{ma}	Molar interaction energy between regions of types m and a
u_0^{ma}	Temperature independent molar interaction energy between regions of types m and a
v^*	Volume occupied by one mol of lattice cells
v	Molar volume of the solution at an given pressure and temperature
$\tilde{v}$	Reduced molar volume
v_s	Molar volume of the solution at infinite dilution at an given pressure and temperature
V	Total volume
val	Any of the three thermodynamic properties
x	Mole fraction
x_s	Mole fraction of solvent
Z	Number of charges
z	Lattice coordination number
zq	Mean number of nearest neighbors

Greek letters

α	Quantity defined by Equation (27)
α,β	Electron-donor and electron-acceptor, respectively
γ	Activity coefficient
$\gamma^{(x)}$	Mean ionic activity coefficient based on mole fraction scale
$\gamma^{(m)}$	Mean ionic activity coefficient based on molality scale
Γ	MSA shielding parameter
ε_0	Permittivity of vacuum
Θ^{ma}	Exponential term in the expression of the most probable distribution
κ	Debye screening parameter
μ	Chemical potential
ν_i^a	Number of regions of type a in the molecule of type i
Ξ^a	Auxiliary symbol defined in Equation (20)
ρ	Liquid density
ξ_3''	Function defined by Equation (29)
σ	Ionic diameter
υ	Total number of ionic charge
ϕ	Volume fraction
Ψ	Characteristic constant of the lattice

Superscripts

A	Anion
Born	Born contribution to EOS
C	Cation
calc	Calculated
D	Dispersive interactions
exp	Experimental
IGM	Ideal Gas Mixture
m	Molality scale
MSA	Mean Spherical Approximation to EOS
MTC	Contribution of the Mattedi-Tavares-Castier EOS
pure	Pure solvent
R	Residual property as defined in Equation (4)
S	Solvent
x	Mole fraction scale

Subscripts

$\pm$	Mean ionic property
$-$	Anion property
$+$	Cation property
∞	Infinite dilution
chg	Charging process of ion in solution
disc	Discharging process of ion in vacuum
mix	Mixture properties

INTRODUCTION

Electrolyte solutions are encountered in many chemical industrial processes such as water desalination, distillation, extraction, solution crystallization, mineral scale formation in steam systems, gas scrubbing, hydrometallurgy and biotechnology according to Pitzer (1973), Loehe and Donohue (1997) and Myers *et al.* (2002). So, thermodynamic models for electrolyte systems have been developed for evaluating the properties needed to design and simulate processes involving electrolytes. Compared to non-electrolyte solutions, electrolyte solutions are more difficult to model because of the presence of dissolved ions. Myers *et al.* (2002) explain these ions can interact with the solvent and with one another by long-range or short-range electrostatic interactions. Both interactions are always present in electrolyte solutions. However, at low electrolyte concentrations, the long-range forces are dominant whereas, at high concentrations, the short-range forces are dominant. Therefore, an accurate model applicable to electrolyte solutions must consider all these interactions.

Several reviews discuss in depth models for electrolyte solutions such as the publications of Friedman (1981), Loehe and Donohue (1997) and Anderko *et al.* (2002). Generally, these models can be classified in two types of engineering-oriented approaches: excess Gibbs energy (g^E) or Helmholtz energy. Some examples based on g^E expressions are the models of:

- Debye and Hückel (1923), who are pioneers in developing models to describe the behavior of electrolyte solutions. Their model considers the ions as charged hard spheres present in a continuum dielectric medium. The ions has fixed diameters values, and the concentration of the solutions must be lower than 0.1 molal (Guggenheim and Turgeon, 1955);
- Pitzer (1973), which can predict the behavior of single solvent solutions;
- Chen and Evans (1986), who extended the Non-Random Two Liquid model (NRTL) to electrolyte solutions;
- Papaiconomou *et al.* (2002), who used the e-NRTL equation, combining the NRTL model with the Born term and the restricted primitive MSA term, in order to describe systems formed by electrolytes and multiple solvents;
- Nasirzadeh *et al.* (2005), who proposed an equation considering the sum of contributions of the Mean Spherical Approximation (MSA) and NRTL, and applied it to obtain the vapor-pressure and osmotic coefficients of aqueous solutions of lithium hydroxide;
- Salimi *et al.* (2005), who combined the Ghotbi-Vera Mean Spherical Approximation (GV-MSA) with two different equations to account for the cation-hydrated diameter, and correlated and predicted mean ionic activity coefficients insingle and mixed electrolyte solutions.

Haghtalab and Mazloumi (2009) assert g^E models are easily applicable to engineering design and also have good accuracy for different electrolyte solutions. However, such models are not suitable for calculating solution densities and activity coefficients as functions of pressure. Models for electrolyte solutions that express the Helmholtz energy as function of temperature, volume and species amounts do not suffer such shortcomings and therefore, provide a more complete description of the systems modeled.

In the case of models based on Helmholtz energy, Wu and Prausnitz (1998) extended the Peng-Robinson EOS using different terms: the SAFT term to account hydrogen bonding and a term to account the electric charging of ions and subsequent ion-ion and ion-solvent interactions. Liu *et al.* (1999) proposed an equation that includes 6 terms: interactions of ion-ion, ion-dipole, dipole-dipole, Lenard-Jones dispersion, hydrogen bond association accounted by the MSA equation and hard sphere repulsion. They investigated 30 aqueous electrolyte solutions, correlating mean ionic activity coefficient using only one adjustable parameter for each salt. Density and mean ionic activity coefficient in mixtures of salts were also predicted. Myers *et al.* (2002) determined mean ionic activity coefficients and osmotic coefficients at 298.15 K for 138 aqueous salt solutions by a three adjustable parameter equation containing a term based on the Peng-Robinson EOS, a Born term and a MSA term. Based on the perturbed-chain statistical associated fluid theory, Cameretti *et al.* (2005) used the equation named ePC-SAFT, which joins the PC-SAFT and the Dubye-Hückel term, to correlate the vapor pressure and the density of 12 salt solutions, considering two adjustable parameters for each ion. Held *et al.* (2008) extended the work done by Cameretti *et al.* correlating densities and mean ionic activity coefficients at 298.15 K and predicting vapor pressures. Inchekel *et al.* (2008) proposed an extension of the Cubic Plus Association (CPA) equation along with Born and MSA terms, in order to calculate the apparent molar volume, mean ionic activity coefficient and osmotic coefficient for 10 aqueous electrolyte solutions considering three ion-specific parameters. Held *et al.* (2008) studied the behavior of systems containing weak electrolytes, correlating densities and mean ionic activity coefficients, using ion-pairing parameters. Lee and Kim (2009) used the equation PC-SAFT along with the primitive MSA term and adjusted 4 ion-specific parameters for

26 aqueous electrolyte solutions, correlating density and mean ionic activity coefficient data at 298.15 K and 1 bar.

The aim of this work is to present an EOS for electrolyte solutions, applicable to calculations of phase equilibrium and thermodynamic properties. This equation uses the Helmholtz approach, including three terms: one related to the Mattedi-Tavares-Castier EOS (MTC EOS) of Mattedi *et al*. (1998), based on the hole-lattice theory and whose partition function is obtained from the generalized van der Waals theory, along with the Born and MSA terms. Due to the combination of the hole-lattice theory with long-range interactions typical of electrolyte solutions, it is named electrolattice EOS. This model is used to calculate vapor pressures, mean ionic activity coefficients, densities and osmotic coefficients of 13 aqueous solutions of strong electrolytes containing salts of type 1:1 (LiCl, LiBr, LiI, NaCl, NaBr, NaI, KCl, KBr, KI, CsCl, CsBr, CsI and RbCl). Two approaches are presented: one considering ion-specific parameters, whose idea is to use parameters for the ions independently of the aqueous solutions they are inserted; the other considering salt-specific parameters, whose goal is to use ionic parameters dependent on the salt that constitutes the aqueous solution. Both kinds of parameters are analyzed in terms of the accuracy of the calculated thermodynamic properties compared to their experimental data.

1 ELECTROLATTICE EQUATION OF STATE

According to the Helmholtz energy (A) approach, it is possible to develop an EOS applicable to electrolytes following the suggestions of Myers *et al*. (2002). In general, they consider a path that starts from the reference state and passes through several intermediate states until reaching the final state that corresponds to the electrolyte solution. This procedure allows the formulation of a model using a path of constant temperature and volume. The change in Helmholtz energy between the final and initial states is equal to the residual Helmholtz energy computed by adding the Helmholtz energy changes between consecutive states along the path. The transition from each state to the next corresponds to adding another type of specific interaction to the system. These changes represent ion-solvent and solvent-solvent physical interactions of short range, association or solvation and long-range ion-ion interactions.

Santos (2010) developed the electrolattice EOS following a four step thermodynamic path (*Fig. 1*), as follows:

- ***step I.*** It is assumed that a reference mixture constituted by charged ions and molecules is in a hypothetical ideal gas state at temperature T and volume V. In the first step, the charges on all ions are removed. The change in Helmholtz energy is accounted by the Born equation for ions in a vacuum, ΔA_{disc}^{Born};
- ***step II.*** The short-range attractive dispersion and repulsive forces due to excluded volume are turned on. Also, self-association of solvent molecules can occur. The MTC EOS is used to calculate the change in Helmholtz energy for this step, ΔA^{MTC};
- ***step III.*** The ions are recharged. The change in Helmholtz energy is accounted by the Born equation for ions in a dielectric solvent, ΔA_{chg}^{Born};
- ***step IV.*** The long-range interactions among the ions in solution are taken into account using the Mean Spherical Approximation (MSA), and the corresponding change in the molar Helmholtz free energy is denoted by ΔA^{MSA}.

The residual Helmholtz energy for forming an electrolyte solution is given by:

$$A(T, V, \mathbf{n}) = A^{MTC}(T, V, \mathbf{n}) + \Delta A^{Born}(T, V, \mathbf{n}) + \Delta A^{MSA}(T, V, \mathbf{n}) \quad (1)$$

wherein

$$A^{MTC}(T, V, \mathbf{n}) = A^{IGM}(T, V, \mathbf{n}) + \Delta A^{MTC}(T, V, \mathbf{n}) \quad (2)$$

$$\Delta A^{Born}(T, V, \mathbf{n}) = \Delta A_{disc}^{Born}(T, V, \mathbf{n}) + \Delta A_{chg}^{Born}(T, V, \mathbf{n}) \quad (3)$$

Equation (1) can be arranged in order to obtain the residual Helmholtz energy in the following manner:

$$A(T, V, \mathbf{n}) - A^{IGM}(T, V, \mathbf{n}) = A^{R}(T, V, \mathbf{n}) = \Delta A^{MTC} + \Delta A^{Born} + \Delta A^{MSA} \quad (4)$$

In these equations, T is the temperature of the system, V is the volume, $\mathbf{n}$ is a vector of the number of moles of the species, A^{IGM} is the Helmholtz energy of the ideal gas mixture that corresponds to the reference state and A^{R} is the residual Helmholtz energy. The term A^{MTC} is the contribution of the MTC EOS to the Helmholtz energy that includes the repulsive and attractive effects, association and the ideal gas contribution, whereas ΔA^{MTC} is the contribution of the MTC EOS to the Helmholtz energy without ideal gas contribution. Expressions for the pressure and chemical potential can be obtained using standard techniques. According to Myers *et al*.

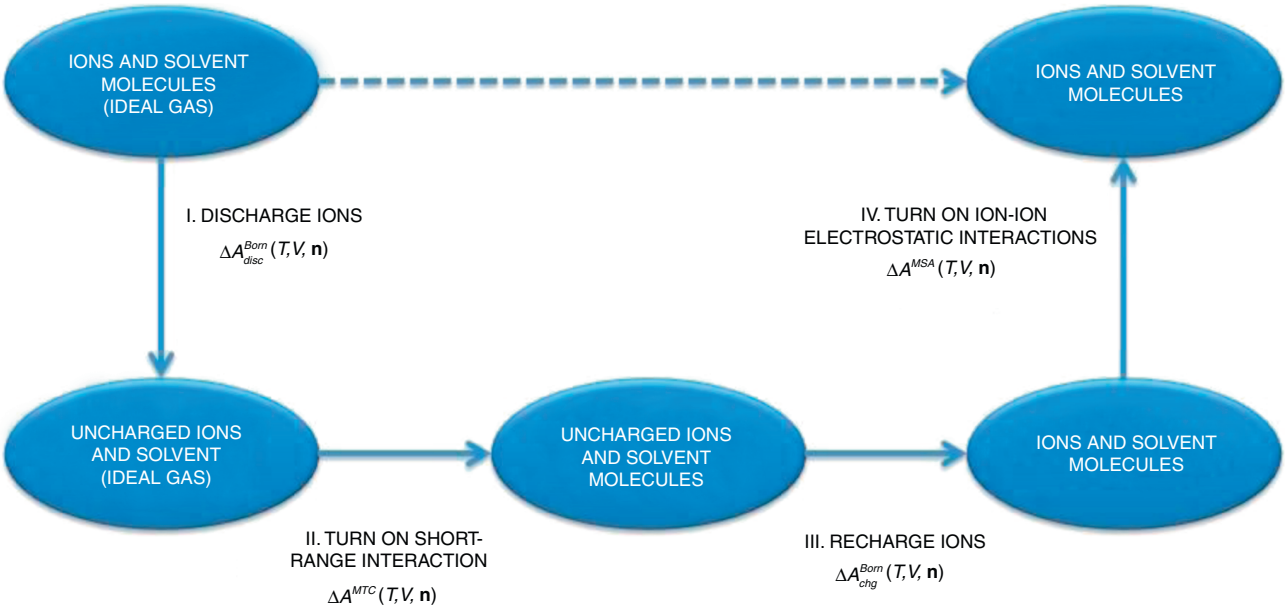

Figure 1

Path to the formation of an electrolyte solution at constant temperature and volume proposed by Myers *et al.* (2002).

(2002), it is possible to obtain the following expression for the fugacity coefficient:

$$\phi_i(T,P,\mathbf{x}) = \frac{1}{Z}\exp\left[\frac{\Delta\mu_i^{MTC}}{RT}\right]\exp\left[\frac{\Delta\mu_i^{Born}}{RT}\right]\exp\left[\frac{\Delta\mu_i^{MSA}}{RT}\right] \tag{5}$$

In the next subsections, the terms that form the electrolattice EOS are presented and discussed.

1.1 Short-Range Contribution (MTC EOS)

In the electrolattice EOS, the short-range interactions between species are accounted for by the MTC EOS, whose Helmholtz energy expression was developed by Mattedi *et al.* (1998). This EOS can be used in three forms: as a molecular model, as a conventional group-contribution model or, as done here, as a region-contribution model, by splitting each molecule in regions. Each molecular region interacts differently with the regions of its neighboring molecules (Santos *et al.*, 2010). The expressions for the pressure and chemical potential derived from this expression for the Helmholtz energy are:

$$\frac{P^{MTC}}{RT} = \frac{1}{v^*}\ln\left[\frac{\tilde{v}}{(\tilde{v}-1)}\right] + \frac{z}{2v^*}\ln\left[\frac{(\tilde{v}-1+q/r)}{\tilde{v}}\right] + \frac{\ell}{r\tilde{v}v^*} - \frac{1}{r\tilde{v}v^*}\cdot\frac{\tilde{v}\Psi(q/r)}{\tilde{v}-1+(q/r)}\sum_{i=1}^{nc}\sum_{a=1}^{ng}x_i\nu_i^aQ^a\ln\left(\frac{\Xi^a-1}{\tilde{v}-1+(q/r)\Xi^a}\right) \tag{6}$$

$$\frac{\mu_i^{MTC}}{RT} = \frac{\mu_i^{IGM}}{RT} + \frac{\Delta\mu_i^{MTC}}{RT} = -\ln f_i(T) - r_i\ln\left[\frac{\tilde{v}-1}{\tilde{v}-1+q/r}\right] + \ln\left[\frac{x_i/r}{\tilde{v}-1+q/r}\right] - \ell_i\ln\left[\frac{\tilde{v}}{\tilde{v}-1+q/r}\right] - \frac{P\tilde{v}v^*\delta_i}{RT} + \frac{\Psi(q/r)(q_i-r_i)}{(\tilde{v}-1+q/r)} + \Psi\sum_{a=1}^{ng}\nu_i^aQ^a\ln\left[\frac{\tilde{v}-1+q/r}{\tilde{v}-1+(q/r)\Xi^a}\right] - \left(\frac{\Psi}{r}\right)\frac{\sum_{i=1}^{nc}\sum_{a=1}^{ng}x_i\nu_i^aQ^a\left[\sum_{m=1}^{ng}\nu_i^m\Theta^{ma}Q^a - r_i\right]}{(\tilde{v}-1+(q/r)\Xi^a)} \tag{7}$$

In Equations (6) and (7), ν_i^a is the number of regions of type a in a molecule of type i, ng is the total number of regions, nc is the number of components, Q^a is the surface area of a region of type a, z is the coordination number ($z = 10$), Ψ is a lattice constant ($\Psi = 1$) and v^* is volume of one mol of cells ($v^* = 5\times10^{-6}$ m^3.mol^{-1}).

The number of external contacts (zq_i), the bulkiness factor (ℓ_i) and the reduced volume ($\tilde{v}$) are:

$$zq_i = \sum_{a=1}^{ng} z\nu_i^aQ^a \tag{8}$$

$$\ell_i = \left(\frac{z}{2}\right)(r_i - q_i) - (r_i - 1) \quad (9)$$

$$\tilde{v} = \frac{v}{r.v^*} \quad (10)$$

$$\delta_i = \frac{r_i(v^* - v_i^*)}{r.v^*} \quad (11)$$

wherein v is the molar volume, $v^* = \sum_{i=1}^{nc} \phi_i v_i^*$ with,

$$\phi_i = \frac{r_i x_i}{\sum_{j=1}^{nc} r_j x_j} \quad (12)$$

The ions are assumed to be spherical and their bulkiness factors are calculated accordingly. We follow Abrams and Prausnitz (1975) in defining the volume (r) and surface area (q) parameters as ratios:

$$r_i = \frac{V_i}{V^*} = \frac{\frac{4\pi}{3} R_i^3}{\frac{4\pi}{3} R^{*3}} = \left(\frac{R_i}{R^*}\right)^3 \quad (13)$$

$$q_i = \frac{A_i}{A^*} = \frac{4\pi R_i^2}{4\pi R^{*2}} = \left(\frac{R_i}{R^*}\right)^2 \quad (14)$$

wherein R_i is the radius of a spherical ion i, V_i is its volume and A_i is its surface area. The corresponding symbols with an asterisk denote the same properties for a lattice cell, assumed to be spherical in Equations (13) and (14). It follows from these equations that, for a spherical ion:

$$q_i = r_i^{2/3} \quad (15)$$

The bulkiness factor is obtained by substituting Equation (15) in Equation (9):

$$\ell_i = \left(\frac{z}{2}\right)\left(r_i - r_i^{2/3}\right) - (r_i - 1) \quad (16)$$

For determining the volume parameter, the ratio between the ion volume and the cell volume is used as follows:

$$r_i = \frac{\pi}{6}\frac{N_a}{v^*}\sigma_i^3 \quad (17)$$

in which σ_i is the diameter of the ion and N_a is the Avogadro's number. Therefore, knowing the ion diameter, it is possible to calculate the volume parameter, the bulkiness factor and the surface area parameter by applying these three equations.

Equations (13) to (17) are exclusively for calculating ion parameters, since the spherical shape is imposed. For the solvent molecule, no physical structure is assumed. Thus, no mathematical relation is proposed to connect the area and volume parameters for the solvent.

The average values of r and zq are:

$$r = \sum_{i=1}^{nc} r_i x_i \quad (18)$$

$$zq = \sum_{i=1}^{nc} zq_i x_i \quad (19)$$

Other symbols present in previous equations are defined as follows:

$$\Xi^a = \sum_{m=1}^{ng} \frac{\sum_{i=1}^{nc} v_i^m x_i Q^m}{q} \Theta^{ma} \quad (20)$$

$$q = \sum_{i=1}^{nc} x_i \sum_{a=1}^{ng} v_i^a Q^a \quad (21)$$

$$\Theta^{ma} = \exp\left[-\frac{u^{ma}}{RT}\right] \quad (22)$$

where u^{ma} is the interaction energy between the m and the a regions, given as:

$$\frac{u^{ma}}{R} = \frac{u_0^{ma}}{R}\left(1 + \frac{B^{ma}}{T}\right) \quad (23)$$

The chemical potential of component i given by Equation (7) is the total contribution, including the ideal gas contribution, which is equal to:

$$\frac{\mu_i^{IGM}(T, V, \mathbf{x})}{RT} = -\ln f_i(T) - \ln\frac{RT}{v^*} - \frac{\delta_i}{r} \quad (24)$$

which is consistent with the MTC model. The difference between Equations (7) and (24) is the residual chemical potential of component i in the MTC model with only repulsive and attractive forces contributions included ($\Delta\mu_i^{MTC}/RT$).

1.2 Born Contribution

In the electrolattice EOS, the Born contribution term accounts for the variation in the Helmholtz energy for discharging an ion in vacuum (ideal gas) and charging it in a solvent. In it, the ions are considered as hard spheres immersed in a continuum with uniform dielectric constant. The Born contribution term to the pressure is:

$$\frac{\Delta P^{Born}}{RT} = -\frac{1}{4\pi D}\frac{N_a e^2}{\varepsilon_0 DRT}\left(\frac{\partial D}{\partial V}\right)_{T,\mathbf{n}} \sum_i \frac{n_i Z_i^2}{\sigma_i} \quad (25)$$

in which e is the unit of elementary charge, ε_0 is the permittivity of vacuum, D is the relative dielectric constant of the solution and Z_i is the number of charge of species i.

The chemical potential of component i due to the Born model is:

$$\frac{\Delta\mu_i^{Born}(T,V,\mathbf{x})}{RT} = \frac{e^2 N_a}{4\pi\varepsilon_0 RT}\frac{Z_i^2}{\sigma_i}\left(\frac{1}{D}-1\right) - \left(\frac{\partial D}{\partial n_i}\right)_{T,V,n_{i\neq j}} \frac{\alpha^2}{4\pi D}\sum_j \frac{n_j Z_j^2}{\sigma_j} \tag{26}$$

in which:

$$\alpha^2 = \frac{e^2 N_a}{\varepsilon_0 DRT} \tag{27}$$

The Born term depends on the relative dielectric constant (D). We use the Pottel model for electrolyte solutions, which is presented by Zuo and Fürst (1997) as:

$$D = 1 + (D_S - 1)\left[\frac{1-\xi_3''}{1+(\xi_3''/2)}\right] \tag{28}$$

wherein:

$$\xi_3'' = \frac{N_a\pi}{6}\sum_i^{ions}\frac{n_i(\sigma_i)^3}{V} \tag{29}$$

Here, D_s is the pure solvent dielectric constant. To evaluate it for pure water, we used the following relation, reported by Zuo and Fürst (1997), for temperatures in Kelvin:

$$D_s = -19.2905 + \frac{2.98145\times10^4}{T} - 1.9678\times10^{-2}T + 1.3189\times10^{-4}T^2 - 3.0\times10^{-7}T^3 \tag{30}$$

1.3 Long-Range Electrostatic Contribution – Mean Spherical Approximation (MSA)

Many published models try to describe the long-range electrostatic contributions of charged species in solution. The MSA has been extensively used to describe such interactions, with different levels of approximation. Instead of solving implicit forms of the MSA iteratively, we opted for the explicit approximation with single effective ion diameter of Harvey *et al.* (1988), with diameter values for cations and anions obtained by Marcus (1988). This form of MSA was successfully used by Myers *et al.* (2002) along with the Peng-Robinson EOS for obtaining mean ionic activity coefficient of many salt solutions. The contribution of this MSA term to the pressure is:

$$\frac{\Delta P^{MSA}}{RT} = \frac{2RT}{3\pi N_a} \times \left[3\Gamma^2 V\left(\frac{\partial\Gamma}{\partial V}\right)_{T,\mathbf{n}}\{2\Gamma\sigma_{mix}+1\} + \Gamma^3\left\{1+\frac{3}{2}\sigma_{mix}\Gamma\right\}\right] \tag{31}$$

wherein,

$$\sigma_{mix} = \frac{\sum_i n_i\sigma_i Z_i^2}{\sum_i n_i Z_i^2} \tag{32}$$

$$\kappa^2 = \frac{e^2 N_a^2}{\varepsilon_0 DRTV}\sum_i n_i Z_i^2 \tag{33}$$

$$\Gamma = \frac{\left(\sqrt{1+2\sigma_{mix}\kappa}-1\right)}{2\sigma_{mix}} \tag{34}$$

in which D is the dielectric constant presented in Equation (28). In these equations, κ is the Debye screening parameter and Γ is the MSA shielding parameter. The contribution of this MSA term to the chemical potential is:

$$\frac{\Delta\mu_i^{MSA}(T,V,\mathbf{x})}{RT} = -\frac{2}{\pi}\Gamma^2 V\left(\frac{\partial\Gamma}{\partial n_i}\right)_{T,V,n_{i\neq j}}\left(1+\frac{3}{2}\sigma_{mix}\Gamma\right) - \frac{2\Gamma^3}{3\pi N_a}\left[\frac{3}{2}V\left\{\Gamma\left(\frac{\partial\sigma_{mix}}{\partial n_i}\right)_{T,V,n_{i\neq j}} + \sigma_{mix}\left(\frac{\partial\Gamma}{\partial n_i}\right)_{T,V,n_{i\neq j}}\right\}\right] \tag{35}$$

2 THERMODYNAMIC PROPERTIES

The relation between the fugacity coefficient and the activity coefficient for an ion of species i and for solvent s can be expressed, respectively, as:

$$\gamma_i^{(x)}(T,P,\mathbf{x}) = \frac{\varphi_i(T,P,\mathbf{x})}{\varphi_i(T,P,x_s\to1)} \tag{36}$$

$$\gamma_s(T,P,\mathbf{x}) = \frac{\varphi_s(T,P,\mathbf{x})}{\varphi_s(T,P)} \tag{37}$$

wherein $\gamma_i^{(x)}(T,P,\mathbf{x})$ is the unsymmetrical activity coefficient of ion i on the mole fraction scale; $\varphi_i(T, P, \mathbf{x})$ is the fugacity coefficient of ion I in the solution; $\varphi_i(T,P,x_s\to1)$ is the fugacity coefficient of ion i at infinite dilution; $\varphi_s(T, P, \mathbf{x})$ is the fugacity coefficient of solvent s in the solution and $\varphi_s(T, P)$ is the fugacity coefficient of pure solvent s.

The activity coefficient of ion i on the molality scale is given by:

$$\gamma_i^{(m)}(T,P,\mathbf{x}) = x_s\left[\frac{\phi_i(T,P,\mathbf{x})}{\phi_i(T,P,x_s\to1)}\right] = \left(\frac{1}{1+vmM_s}\right)\left[\frac{\phi_i(T,P,\mathbf{x})}{\phi_i(T,P,x_s\to1)}\right] \tag{38}$$

wherein x_s is the molar fraction of the solvent; v is the sum of stoichiometric coefficients of the ions in the salt molecules, in this work, $v = 2$ since the employed salts are 1:1; m is the molality; and M_s is the molecular weight of the solvent in kg.mol^{-1}. Expressions for the mean ionic activity coefficient and for the osmotic coefficient are available in several references (*e.g.*, Myers *et al.*, 2002).

3 PARAMETER FITTING

Solutions containing aqueous single strong 1:1 electrolytes are formed by three species: solvent, cation (C) and anion (A). Since the MTC EOS term is present in the electrolattice EOS, according to Ehlker and Pfenning (2002) and Mattedi *et al.* (1998), it is convenient to split the solvent molecule in three regions: an electron-donor (α), an electron-acceptor (β) and a dispersion region (D).

Once the aim of this work is to determine thermodynamic properties of electrolyte solutions, the first step toward this goal is to obtain the parameters for pure water. As in the MTC EOS, the electrolattice EOS uses seven parameters to represent pure polar solvents. These parameters were obtained by simultaneous fit of liquid density data and pressure at saturation, obtained from the DIPPR correlation (American Institute of Chemical Engineers, 2007), in the temperature range from 292.84 to 489.67 K. To reduce the number of adjustable solvent parameters, all region-region interactions, except that between α and β regions, are assumed to be dispersion interactions, numerically equal (${u_0}^{D-D}/R$). These interactions are assumed to be temperature dependent, with $B^{\alpha\text{-}\alpha} = B^{\alpha\text{-}D} = B^{\beta\text{-}\beta} = B^{\beta\text{-}D} = B^{D\text{-}D}$. Also for reducing the number of adjustable parameters, the interaction between α and β regions, which refers to the hydrogen bond, is considered to be temperature independent ($B^{\alpha\text{-}\beta} = 0$). Table 1 shows the parameters for water used in this paper.

When an electrolyte solution of a single salt and a solvent is modeled by the electrolattice EOS, there are five regions that interact with one another (three for the solvent (α, β, D), one for the cation (C) and one for the anion (A)). Each of these interactions is, in principle, supposed to follow Equation (23) and there would be 18 adjustable parameters in such a solution: 9 parameters (u_0^{ma}/R) and 9 parameters B^{ma}. This is inconvenient in an engineering-oriented model and we adopted simplifications to reduce the number of adjustable parameters. We assumed the interactions between water regions and each charged species are equal, *i.e.*:

$$\frac{u_0^{\alpha-C}}{R} = \frac{u_0^{\beta-C}}{R} = \frac{u_0^{D-C}}{R} = \frac{u_0^{solvent-C}}{R} \quad (39)$$

$$\frac{u_0^{\alpha-A}}{R} = \frac{u_0^{\beta-A}}{R} = \frac{u_0^{D-A}}{R} = \frac{u_0^{solvent-A}}{R} \quad (40)$$

These interactions are assumed to be temperature independent; therefore, the B^{ma} term of Equation (23) is neglected as follows:

$$B^{\alpha-C} = B^{\beta-C} = B^{D-C} = B^{\alpha-A} = B^{\beta-A} = B^{D-A} = 0 \quad (41)$$

Two assumptions are made about the interactions between ionic species. Following Zuo *et al.* (2000), the short-range interaction between ions with the same charge is neglected once the repulsion between the species is strong, therefore:

$$\frac{u^{A-A}}{R} = \frac{u^{C-C}}{R} = 0 \quad (42)$$

Also, according to Lee and Kim (2009), it is possible to neglect the short-range interactions between ions of different charges in solution, *i.e.*:

$$\frac{u^{A-C}}{R} = \frac{u^{C-A}}{R} = 0 \quad (43)$$

With these simplifications, each ion has only one adjustable parameter and yet, the electrolattice EOS gives good results.

To calculate the vapor pressure of electrolyte solutions, it is assumed the vapor phase only contains water. Also, all the salts are strong electrolytes, which fully dissociate in solution into cations and anions. Then, for each data point, there is only one phase equilibrium

TABLE 1
Water parameters

Compound	Q^D	Q^α	Q^β	r	$\frac{u_0^{D-D}}{R}$ (K)	B^{D-D} (K)	$\frac{u_0^{\alpha-\beta}}{R}$ (K)
Water	0.857715	0.712207	0.172331	2.14949	−535.864	700.671	−2 625.69

equation, the isofugacity equation for water, which is solved to find the vapor pressure at a given temperature.

In this work, the experimental data set for vapor pressure is composed by: Hubert *et al*. (1995), who obtained data for NaCl in a temperature range from 293.15 to 363.15 K; for LiCl, LiBr and LiI, the work of Patil *et al*. (1990) was used and, for other salts, the work of Patil *et al*. (1991) was used, both in the temperature range from 303.15 K to 343.15 K. For mean ionic activity coefficients and osmotic coefficients, the data were obtained from Robinson and Stokes (1949) and Lobo and Quaresma (1989) at atmospheric pressure and 298.15 K.

Considering the parameters obtained for the pure solvent and the set of simplifications for the ions, the number of adjustable parameters in a single-salt aqueous solution is reduced to two: $(u_0^{solvent-C}/R)$ and $(u_0^{solvent-A}/R)$. Different approaches are used to determine these energy interactions: the first considers the parameters as salt-specific, in which, these two parameters are simultaneously obtained for each salt; the second approach considers the parameters as ion-specific, which means that the energy interaction between water and an ion must always be the same, independently of the salt it takes part. The ion-specific approach is more complex compared to the salt-specific approach since more parameters need to be fitted at the same time. Following Held *et al*. (2008), we first determined the parameters for a basic set of salts, composed by three cations (Na^+, K^+, Li^+) and three anions (Br^-, Cl^-, I^-), corresponding to nine single-salt aqueous solutions. In this initial fitting, 6 parameters were simultaneously obtained using 368 data points for vapor pressure and 208 data points for mean ionic activity coefficient. Then, the anion parameters obtained previously were fixed to determine the Cs^+ parameters, using experimental data of CsBr, CsCl and CsI aqueous solutions. Likewise, the Rb^+ parameters were determined by correlating the experimental data of RbCl.

For both approaches previously mentioned, the adjustable parameters were determined using the Excess Gibbs Energy Models and Equations of State (XSEOS) package, an Excel® add-in developed by Castier and Amer (2011), by minimizing the Objective Function (*OF*):

$$OF = \sum_{i=1}^{Np} \left(\frac{P_i^{calc} - P_i^{exp}}{P_i^{calc}} \right)^2 + \sum_{i=1}^{Np} \left(\frac{\gamma_{\pm i}^{calc} - \gamma_{\pm i}^{exp}}{\gamma_{\pm i}^{calc}} \right)^2 \quad (44)$$

in which P_i^{calc} and $\gamma_{\pm i}^{calc}$ denote calculated values for vapor pressure and mean ionic activity coefficient, respectively; P_i^{exp} and $\gamma_{\pm i}^{exp}$ are the corresponding experimental values; *Np* is the number of points.

4 RESULTS AND DISCUSSION

The volume, the bulkiness and the surface area parameters for ions are calculated using Equations (15-17). Marcus (1988) determined the ionic diameter of several cations and anions in aqueous solutions, which are used instead of Pauling-type crystal ionic diameters (Pauling, 1927). The diameter values used in our model are presented in Table 2.

The parameters fitted by the salt-specific and ion-specific approaches are shown in Tables 3 and 4,

TABLE 2
Ionic diameters according to Marcus (1988)

Ion	σ_i (Å)
Li^+	1.42
Na^+	1.94
K^+	2.82
Rb^+	3.00
Cs^+	3.46
Cl^-	3.60
Br^-	3.96
I^-	4.50

TABLE 3
Salt-specific parameters

Salt	$\frac{u_0^{solvent-C}}{R}$ (K)	$\frac{u_0^{solvent-A}}{R}$ (K)
LiCl	−2 787.85	−1 808.60
LiBr	−2 731.22	−1 926.85
LiI	−2 725.82	−1 799.22
NaCl	−808.08	−2 110.77
NaBr	−2 482.99	−988.07
NaI	−2 448.56	−1 416.51
KCl	−612.10	−613.18
KBr	−97.54	−1 189.34
KI	−482.85	−459.96
CsCl	−2 134.57	3 635.93
CsBr	−2 171.67	5 990.57
CsI	−2 233.42	4 487.87
RbCl	−1 916.47	−142.84

respectively. In Table 5, the values for the Average Relative Deviation (ARD(%)), calculated by Equation (45),

TABLE 4
Ion-specific parameters

Ion	$\frac{u_0^{solvent-ion}}{R}$ (K)
Li^+	−2831.67
Na^+	−2448.74
K^+	−24.74
Rb^+	−27.14
Cs^+	626.51
Cl^-	−1461.32
Br^-	−1488.42
I^-	−1321.96

for vapor pressure, mean ionic activity coefficient and osmotic coefficient of each salt solution are presented. These outcomes are shown in Table 5 for both fitting approaches, as SSP for salt-specific parameters, and ISP for ion-specific parameters.

$$ARD(\%) = \frac{100}{Np}\sum_{i=1}^{Np}\left|\frac{val_i^{calc} - val_i^{\exp}}{val_i^{\exp}}\right| \qquad (45)$$

In Equation (45), val_i^{calc} and $val_i^{\exp}$ represent the calculated and experimental values of vapor pressure, mean ionic activity coefficient or osmotic coefficient. Table 5 shows the electrolattice EOS with salt-specific and ion-specific parameters can correlate vapor pressure satisfactorily, with average of ARD values equal to 1.74% and 1.84%, respectively. A comparison of our results with those obtained by Held *et al.* (2008) for the same salts shows that their average ARD for vapor pressure is 4.48%.

TABLE 5
Average Relative Deviation (ARD(%)) of 1:1 salt thermodynamic properties considering two parameter fitting approaches

Salt	Vapor pressure ARD(%)				Mean ionic activity coefficient ARD(%)				Osmotic coefficient ARD(%)			
	Np	m_{max} (mol/kg)	SSP	ISP	*Np*	m_{max} (mol/kg)	SSP	ISP	*Np*	m_{max} (mol/kg)	SSP	ISP
LiCl	20[2]	7.8	2.76	2.72	22[4]	6.0	4.56	4.44	22[5]	6.0	2.97	2.92
LiBr	20[2]	7.0	2.29	2.39	23[4]	6.0	6.98	6.92	23[5]	6.0	4.03	4.02
LiI	25[2]	7.5	2.12	2.12	17[4]	3.0	2.49	3.51	17[5]	3.0	1.67	2.30
NaCl	133[1]	5.4	2.16	1.97	35[4]	6.0	1.70	1.77	35[5]	6.0	1.29	1.37
NaBr	30[3]	8.0	1.71	2.07	19[4]	4.0	1.24	1.62	19[5]	4.0	0.80	1.12
NaI	40[3]	8.4	1.48	1.33	31[4]	8.0	2.32	2.24	31[5]	8.0	1.50	1.44
KCl	30[3]	4.3	1.72	1.51	20[4]	4.5	0.56	3.49	20[5]	4.5	0.42	1.54
KBr	30[3]	4.3	1.02	1.04	21[4]	5.0	0.49	0.53	21[5]	5.0	0.41	0.36
KI	40[3]	5.6	1.62	2.15	20[4]	4.5	0.43	2.56	20[5]	4.5	0.31	1.52
CsCl	40[3]	8.6	1.21	3.19	21[4]	5.0	2.10	5.83	21[5]	5.0	1.40	4.73
CsBr	30[3]	5.9	2.16	1.11	21[4]	5.0	1.83	3.24	21[5]	5.0	1.29	2.24
CsI	25[3]	2.6	1.20	1.21	17[4]	3.0	0.62	10.88	17[5]	3.0	0.62	4.57
RbCl	30[3]	6.5	1.21	1.13	21[4]	5.0	1.44	1.23	21[5]	5.0	1.01	0.87
Average	-	-	1.74	1.84	-	-	2.06	3.71	-	-	1.36	2.23

[1] Hubert *et al.* (1995) in temperature range 293.15-363.15 K.
[2] Patil *et al.* (1991) in temperature range 303.15-343.15 K.
[3] Patil *et al.* (1990) in temperature range 303.15-343.15 K.
[4] Robinson and Stokes (1949) at temperature 298.15 K.
[5] Lobo and Quaresma (1989) at temperature 298.15 K.
SSP: Salt-Specific Parameters.
ISP: Ion-Specific Parameters.

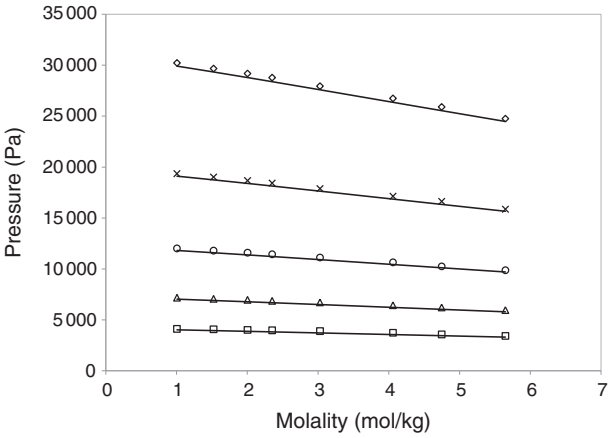

Figure 2

Vapor pressure of KI in water at 303.15 K (□), 313.15 K (Δ), 323.15 K (○), 333.15 K (×) and 343.15 K (◇), obtained by Patil *et al.* (1991). The full line (—) represents the electrolattice model considering ion-specific parameters.

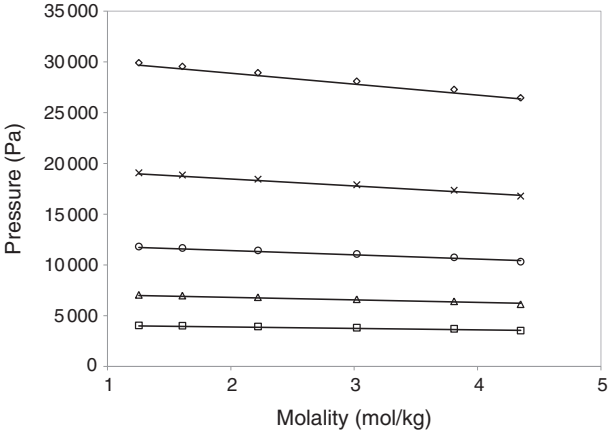

Figure 3

Vapor pressure of KBr in water at 303.15 K (□), 313.15 K (Δ), 323.15 K (○), 333.15 K (×) and 343.15 K (◇), obtained by Patil *et al.* (1991). The full line (—) represents the electrolattice model considering ion-specific parameters.

Figures 2 and 3 present the vapor pressures of aqueous solutions containing KI and KBr, respectively, as function of molality in the temperature range from 303.15 K to 343.15 K, using ion-specific parameters. The results with the salt-specific parameters, not shown in these figures, are similar. With both fitting approaches, the results of the model are in good agreement with the experimental data.

For the mean ionic activity coefficient data (*Tab. 5*), in general, the salt-specific parameters correlate the

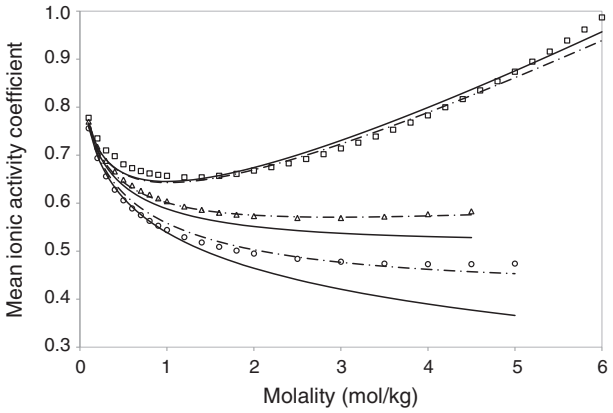

Figure 4

Mean ionic activity coefficient of NaCl (□), KCl (Δ) and CsCl (○) in water at 1 atm and 298.15 K, obtained from Lobo and Quaresma (1989). The lines represent the electrolattice model considering salt-specific parameters (–·–) and ion-specific parameters (—).

experimental data more adequately than the ion-specific parameters, except for RbCl. The average ARD for such approaches are 2.06 % and 3.71 %, respectively. The results obtained for LiBr and CsI are higher compared to other salts modeled by ion-specific parameters, and their ARD values are 6.92% and 10.88 %, respectively. In Figure 4, it is possible to observe that the mean ionic activity coefficient is underestimated for KCl and CsCl at 298.15 K and at atmospheric pressure, when ion-specific parameters are used. Also in Figure 4, it is possible to observe that for salts whose anion is Cl^-, the larger is the diameter of the cation, the lower is the mean ionic activity coefficient in all the molality range. In Figure 5, salts containing Br^- as the anion are presented. Also in this set of salts, the mean ionic activity coefficient decreases as the cation size increases, in the sequence NaBr > KBr > CsBr. Figure 5 also shows that the electrolattice EOS can match the experimental mean ionic activity coefficient satisfactorily with the parameters fitted by both approaches.

The osmotic coefficient data of aqueous solutions, using the ion-specific and the salt-specific methods, are presented in Figure 6. The average ARD is 1.36% for salt-specific approach and 2.23% for ion-specific approach. This thermodynamic property was not directly used for parameter fitting but the mean ionic activity coefficient is analytically related to the osmotic coefficient *via* the Gibbs-Duhem equation (a complete formulation about this relation can be found in Prausnitz *et al.*, 1999). For aqueous solutions containing NaBr, KBr and RbCl, results using parameters fitted

with the salt-specific and ion-specific approaches are in good agreement with experimental data. For RbCl at high concentrations, the parameters adjusted by both approaches cause underestimation of the osmotic coefficients compared to the experimental data.

It is not possible to observe a trend in the salt-specific parameters of Table 3. Generally, all the parameters have negative values, except the ones obtained for the salts whose cation is Cs^+, in which the energy interaction between the solvent and the anion is positive.

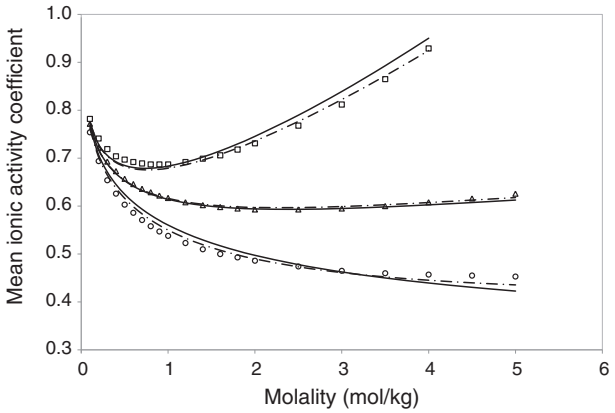

Figure 5

Mean ionic activity coefficient of NaBr (□), KBr (Δ) and CsBr (○) in water at 1 atm and 298.15 K, obtained from Lobo and Quaresma (1989). The lines represent the electrolattice model considering salt-specific parameters (–·–) and ion-specific parameters (—).

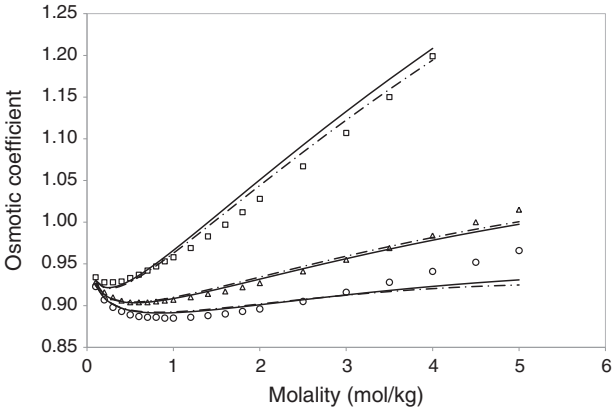

Figure 6

Osmotic coefficient of NaBr (□), KBr (Δ) and RbCl (○) in water at 1 atm and 298.15 K, obtained from Lobo and Quaresma (1989). The lines represent the electrolattice model considering salt-specific parameters (–·–) and ion-specific parameters (—).

TABLE 6

Average Relative Deviation (ARD (%)) of predicted density for 1:1 salts considering the parameters of ion-specific approach

Salt	$Np^{(1)}$	m_{max} (mol/kg)	T range (K)	Density ARD(%)
LiCl	23	13.80	298.15-373.15	7.43
LiBr	16	13.18	298.15-343.34	7.52
LiI	15	8.37	298.15-343.34	7.14
NaCl	45	0.96	298.15-328.15	2.16
NaBr	37	8.00	298.15-328.15	4.06
NaI	20	11.29	298.15-313.15	6.00
KCl	28	3.61	298.15-423.15	3.92
KBr	37	1.20	298.15-368.15	4.06
KI	36	1.00	298.15-368.15	1.63
CsCl	27	8.00	298.15-328.15	6.84
CsBr	18	4.18	298.15-343.34	8.36
CsI	15	2.90	298.15-343.34	5.84
RbCl	25	6.00	298.15-328.15	5.16

(1) Experimental data obtained from Lobo and Quaresma (1989).

On the other hand, the values of ion-specific parameters of Table 4 tend to increase with cation diameter. Potassium and rubidium do not follow this trend but have similar parameters, inside the range set by the sodium and cesium parameters. For the anion parameters, no trend appears in Table 4. The interaction parameter for cesium in Table 4 is positive, suggesting short range repulsion.

With the ion-specific parameters of Table 4, the electrolattice EOS was also used to predict density, mean ionic activity coefficient and osmotic coefficient at temperatures other than 298.15 K and vapor pressures of binary salt solutions.

Density values were predicted for 13 salts considering 342 experimental data points, obtained from Lobo and Quaresma (1989). The results are presented in Table 6. The lowest values for ARD were obtained for KI, NaCl and KCl, as 1.63%, 2.16% and 3.92%, respectively. Compared to Cameretti *et al.* (2005) and Held *et al.* (2008), our results for density are not as accurate as theirs, which are generally lower than 1.0%. A possible reason is that, unlike them, we did not use density data for parameter fitting. Their inclusion in the objective function might have improved the correlation of density data. However, it is important to note that even predicting such results, the electrolattice EOS can describe the correct tendency for the density in all the electrolyte solutions.

For the predictions of mean ionic activity and osmotic coefficients at different temperatures, whose results are presented in Table 7, 267 and 192 data points, respectively, were obtained from Lobo and Quaresma (1989). The average of the ARD values is 4.64% for mean ionic activity coefficient and 3.73% for osmotic coefficient. The best prediction was obtained for NaBr with the ARD values of 2.10% at 273.15 K and 2.45% at 313.15 K. For other salts, such as NaCl, KCl and KBr, the higher the temperature, the larger are the ARD values. For LiCl and CsCl, at any temperature the deviation obtained is higher than 5.0%, indicating that the model cannot predict the thermodynamic property accurately for these solutions. For the osmotic coefficient all the ARD values are below 5.0%, except for CsCl, whose ARD is 7.66% at 323.15 K. For this thermodynamic

TABLE 7
Average Relative Deviation (ARD (%)) of predicted mean ionic activity and osmotic coefficients at different temperatures considering ion-specific parameters

Salt	$Np^{(A)}$	m_{max} (mol/kg)	T (K)	Mean ionic activity coefficient ARD(%)	Osmotic coefficient ARD(%)
LiCl	22	6.0	273.15	11.06	4.55
	22	6.0	323.15	8.81	3.74
LiBr	17	1.1	283.15	2.95	*NA*
NaCl	23	6.0	273.15	2.27	2.01
	23	6.0	323.15	5.88	4.56
NaBr	12	4.0	273.15	2.10	*NA*
	12	4.0	313.15	2.45	*NA*
KCl	22	6.0	273.15	2.03	1.37
	17	1.1	283.15	0.46	*NA*
	22	6.0	323.15	5.17	3.62
KBr	17	1.1	283.15	1.28	*NA*
	14	4.0	333.15	4.62	1.90
CsCl	22	6.0	273.15	5.09	4.15
	22	6.0	323.15	10.79	7.66
Average	-	-	-	4.64	3.73

[(A)] The number of experimental data points is the same for both mean ionic activity and osmotic coefficients, except when the data for osmotic coefficient is Not Available (NA). All experimental data were obtained from Lobo and Quaresma (1989).

TABLE 8
Prediction of vapor pressure of mixtures containing two salts using the ion-specific parameters

Salts	*Np*	*T* range (K)	Vapor pressure ARD(%)
NaCl + KCl	10[(1)]	278.15-323.15	3.96
KBr + KCl	10[(1)]	278.15-323.15	1.93
KI + KCl	10[(1)]	278.15-323.15	5.06
NaBr + KCl	25[(2)]	303.15-333.15	0.78
NaCl + KBr	25[(2)]	303.15-333.15	0.74

[(1)] Apelblat and Korin (2009); [(2)] Hsu *et al*. (2003).

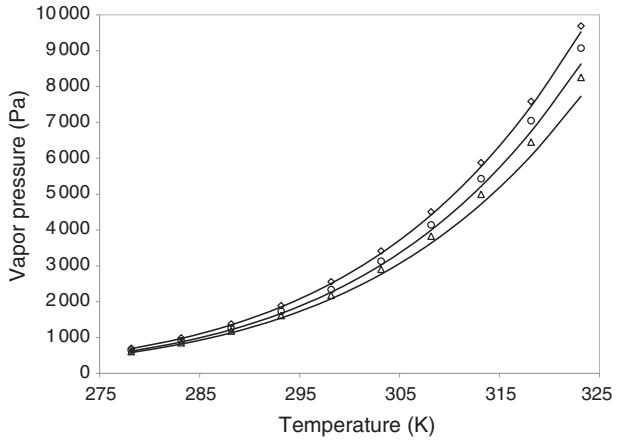

Figure 7

Vapor pressure prediction of saturated solutions of KCl + KBr (□), NaCl + KCl (Δ) and KCl + KI (○) in water, obtained from Apelblat and Korin (2009). The line represents the electrolattice model considering ion-specific parameters (—).

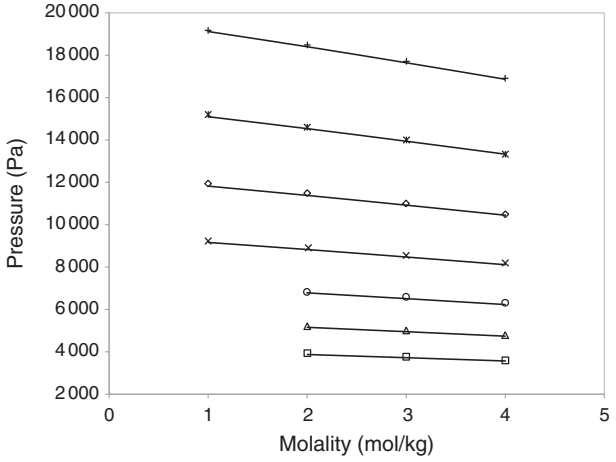

Figure 8

Vapor pressure prediction of NaBr + KCl in water at 303.15 K (□), 308.15 K (Δ), 313.15 K (○), 318.25 K (×), 323.15 K (◇), 328.15 K (*) and 333.15 K (+), obtained from Hsu *et al*. (2003). The line represents the electrolattice model considering ion-specific parameters (—).

property, the prediction is acceptable in the temperature range of each salt.

Predictions of vapor pressure considering binary salt solutions were also analyzed. For solutions composed by NaCl + KCl, KBr + KCl and KI + KCl the experimental data were from Apelblat and Korin (2009), obtained at saturation. For NaBr + KCl and NaCl + KBr, the data were obtained from Hsu *et al*. (2003) at a molality range from 1 to 4 molal and temperature range from 303.15 K to 333.15 K. Table 8 sums up the results for such predictions and Figures 7-9 display the corresponding plots. For the three first solutions, the ARD values are slightly higher than for the other two since the molality is high throughout the temperature range and the model tends to be not so accurate at such condition. For the other two solutions, the predictions are very good in the temperature range from 303.15 to 333.15 K. It should be noted that no parameter fitting is needed when applying the electrolattice EOS to predict vapor pressures of aqueous solutions of multiple salts.

CONCLUSIONS

In this work, the electrolattice equation of state was used to model the thermodynamic properties of aqueous solutions of strong 1:1 electrolytes. The ion volume and surface area parameters used in this EOS were evaluated from ionic diameter data. Experimental data for vapor pressure and mean ionic activity coefficients were used

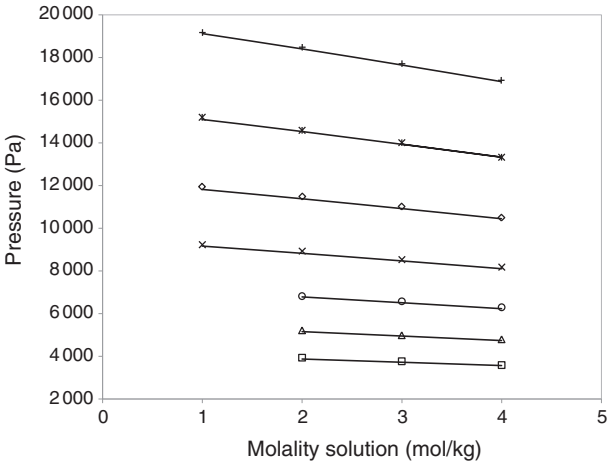

Figure 9

Vapor pressure prediction of NaCl + KBr in water at 303.15 K (□), 308.15 K (Δ), 313.15 K (○), 318.25 K (×), 323.15 K (◇), 328.15 K (*) and 333.15 K (+), obtained from Hsu *et al.* (2003). The line represents the electrolattice model considering ion-specific parameters (—).

to fit the water-ion parameters of the model by using the salt-specific and ion-specific approaches. The results for these two properties are generally in good agreement with experimental values. The results for osmotic coefficient, which was not directly used in the objective function, are also in good agreement with experimental data. Predictions of density, mean ionic activity coefficient and osmotic coefficient at temperatures other than 298.15 K and vapor pressure of binary salt solutions, considering ion-specific parameters, were fairly accurate.

Comparing all the thermodynamic properties, the salt-specific approach tends to produce more accurate correlations. This approach can be useful for specialized applications involving a single salt. However, to develop the model for general applications, the ion-specific approach is the way forward because its parameters can be used for different salts. It is more challenging because the parameters of several ions, cations and anions, are fitted at the same time, often using hundreds of data points. Also, these parameters represent a compromise solution that tries to capture the behavior of multiple properties of multiple systems. In such calculations, even with appropriate minimization methods, started from different initial estimates, the occurrence of local minima in the objective function cannot be ruled out and it is not possible to guarantee a perfect, simultaneous fit of all the thermodynamic properties for all salts. Thus, their ARD values can be low for some salts and high for others. Overall, these results are promising and motivate additional investigations of this model's performance in future work.

ACKNOWLEDGMENTS

The participation of R. Mathew in this work was made possible by UREP grant # 10-124-2-039 from the Qatar National Research Fund (a member of Qatar Foundation). The statements made herein are solely the responsibility of the authors.

REFERENCES

Abrams D.S., Prausnitz J.M. (1975) Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems, *AIChE J.* **21**, 116-127.

American Institute of Chemical Engineers, Design Institute for Physical Properties Research, DIPPR, 2007.

Anderko A., Wang P., Rafal M. (2002) Electrolyte solutions: From thermodynamic and transport property models to the simulation of industrial processes, *Fluid Phase Equilib.* **194-197**, 123-142.

Apelblat A., Korin E. (2009) Temperature dependence of vapor pressures over saturated aqueous solutions at invariant points of the NaCl + KCl + H_2O, NaCl + $NaNO_3$ + H_2O, KCl + KBr + H_2O, KCl + KI + H_2O, KCl + KNO_3 + H2O and KCl + K_2SO_4 + H_2O systems, *J. Chem., Eng. Data* **54**, 1619-1624.

Cameretti L.F., Sadowski G., Mollerup J.M. (2005) Modeling of aqueous electrolyte solutions with perturbed-chain statistical associated fluid theory, *Ind. Eng. Chem. Res.* **44**, 3355-3362.

Castier M., Amer M.M. (2011) XSEOS: An evolving tool for teaching chemical engineering thermodynamics, *Educ. Chem. Eng.* **6**, e62-e70.

Chen C.C., Evans L.B. (1986) A local composition model for the excess Gibbs energy of aqueous electrolyte systems, *AIChE J.* **32**, 444-454.

Debye P., Hückel E. (1923) Zur Theorie der Elektrolyte, *Physik Z.* **24**, 185.

Ehlker G.H., Pfenning A. (2002) Development of GEQUAC as a new group contribution method for strongly non-ideal mixtures, *Fluid Phase Equilib.* **203**, 53-69.

Friedman H.L. (1981) Electrolyte solutions at equilibrium, *Ann. Rev. Phys. Chem.* **32**, 179.

Guggenheim E.A., Turgeon J.C. (1955) Specific interaction of ions, *Trans. Faraday Soc.* **51**, 747-761.

Haghtalab A., Mazloumi S.H. (2009) A square-well equation of state for aqueous strong electrolyte solutions, *Fluid Phase Equilib.* **285**, 96-104.

Harvey A.H., Copeman T.W., Prausnitz J.M. (1988) Explicit approximations to the mean spherical approximation for electrolyte systems with unequal ion sizes, *J. Phys. Chem.* **92**, 6432-6436.

Held C., Cameretti L.F., Sadowski G. (2008) Modeling aqueous electrolyte solutions. Part 1. Fully dissociated electrolytes, *Fluid Phase Equilib.* **270**, 87-96.

Hsu H.-L., Wu Y.-C., Lee L.-S. (2003) Vapor pressures of aqueous solutions with mixed salts of NaCl + KBr and NaBr + KCl, *J. Chem. Eng. Data* **48**, 514-518.

Hubert N., Gabes Y., Bourdet J.-B., Schuffenecker L. (1995) Vapor pressure measurements with a nonisothermal static method between 293.15 and 363.15 K for electrolyte solutions. Application to the H_2O + NaCl system, *J. Chem. Eng. Data* **40**, 891-894.

Inchekel R., Hemptinne J.-C., Fürst W. (2008) The simultaneous repetition of dielectric constant, volume and activity coefficient using an electrolyte equation of state, *Fluid Phase Equilib.* **271**, 19-27.

Lee B.-S., Kim K.-C. (2009) Modeling of aqueous electrolyte solutions based on PC-SAFT incorporated with primitive MSA, *Korean J. Chem. Eng.* **26**, 1733-1747.

Liu W.-B., Li Y.-G., Lu J.-F. (1999) A new equation of state for real aqueous ionic fluids based on electrolyte perturbation theory, mean spherical approximation and statistical associating fluid theory, *Fluid Phase Equilib.* **158-160**, 595-606.

Lobo V.M.M., Quaresma J.L. (1989) *Handbook of electrolyte solutions, Part A and B*, Elsevier, Amsterdam.

Loehe J.R., Donohue M.D. (1997) Recent advances in modeling thermodynamic properties of aqueous strong electrolyte systems, *AIChE J.* **43**, 180-195.

Marcus Y. (1988) Ionic radii in aqueous solutions, *Chem. Rev.* **88**, 1475-1498.

Mattedi S., Tavares F.W., Castier M. (1998) Group contribution equation of state based on the lattice fluid theory: Alkane-alkanol systems, *Fluid Phase Equilib.* **142**, 33-54.

Myers J.A., Sandler S.I., Wood R.H. (2002) An equation of state for electrolyte solutions covering wide ranges of temperature, pressure and composition, *Ind. Eng. Chem. Res.* **41**, 3282-3297.

Nasirzadeh K., Neueder R., Kunz W. (2005) Vapor Pressures and Osmotic Coefficients of Aqueous LiOH Solutions at Temperatures Ranging from 298.15 to 363.15 K, *Ind. Eng. Chem. Res.* **44**, 3807-3814.

Papaiconomou N., Simonin J.-P., Bernard O., Kunz W. (2002) MSA NRTL model for the description of the thermodynamic properties of electrolyte solutions, *Phys. Chem. Chem. Phys.* **4**, 4453-4443.

Patil K.R., Tripathi A.D., Pathak G., Katti S.S. (1990) Thermodynamic properties of aqueous electrolyte solutions. 1. Vapor pressure of aqueous solutions of LiCl, LiBr and LiI, *J. Chem. Eng. Data* **35**, 166-168.

Patil K.R., Tripathi A.D., Pathak G., Katti S.S. (1991) Thermodynamic properties of aqueous electrolyte solutions. 2. Vapor pressure of aqueous solutions of NaBr, NaI, KCl, KBr, KI, RbCl, CsCl, CSBr, CsI, $MgCl_2$, $CaCl_2$, $CaBr_2$, CaI_2, $SrCl_2$, $SrBr_2$, SiI_2, $BaCl_2$ and $BaBr_2$, *J. Chem. Eng. Data* **36**, 225-230.

Pauling L. (1927) The sizes of ions and structure of ionic crystals, *J. Am. Chem. Soc.* **49**, 3, 765-790.

Pitzer K.S. (1973) Thermodynamics of electrolytes. I. Theoretical basis and general equations, *J. Phys. Chem.* **77**, 268-277.

Prausnitz J.M., Lichtenthaler R.N., Azevedo E.G. (1999) *Molecular thermodynamics of fluid-phase equilibria*, Chapter 9, Section 4, Prentice Hall PTR, Upper Saddle River.

Robinson R.A., Stokes R.H. (1949) Tables of osmotic and activity coefficients of electrolytes in aqueous solutions at 25°C, *Trans. Faraday Soc.* **45**, 616-624.

Samili H.R., Taghikhani V., Ghotbi C. (2005) Application of the GV-MSA model to the electrolyte solutions containing mixed salts and mixed solvents, *Fluid Phase Equilib.* **231**, 67-76.

Santos J.P.L. (2010) Equilíbrio de fases de misturas polares e iônicas *via* equação de estado baseada em modelo de rede, *D.Sc. Thesis*, Universidade Federal do Rio de Janeiro.

Santos J.P.L., Tavares F.W., Castier M. (2010) Vapor-liquid equilibrium calculations for refrigerant mixtures with the Mattedi-Tavares-Castier EOS, *Fluid Phase Equilib.* **296**, 133-139.

Wu J., Prausnitz J.M. (1998) Phase equilibria for systems containing hydrocarbons, water and salt: an extended Peng-Robinson equation of state, *Ind. Eng. Chem. Res.* **37**, 1634-1643.

Zuo J.Y., Zhang D., Fürst W. (2000) Predicting LLE in mixed-solvent electrolyte systems by an electrolyte EOS, *AIChE J.* **46**, 2318-2329.

Zuo Y.-X., Fürst W. (1997) Prediction of vapor pressure for nonaqueous electrolyte solutions using an electrolyte equation of state, *Fluid Phase Equilib.* **138**, 87-104.

Final manuscript received in November 2012
Published online in May 2013